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EVALUATION OF LOCALLY AVAILABLE RAW MATERIAL IN THE NATURAL RUBBER INDUSTRY*

PART I — GRAPHITE

BY

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INTRODUCTION

It is well known that graphite, though it is another form of carbon, does not have the reinforcing quality of carbon black when mixed with rubber. Recent evidence indicates that in both carbon black and graphite the carbon atoms are chemically bound together in plane hexagonal networks called layer planes. In graphite these layer planes are evenly spaced in parallel layers giving a crystallite structure where the first layer corresponds to the third and then the fifth and so on. In carbon black the time of formation is short and the arrangement is less ordered. The carbon atoms are still arranged in parallel hexagonal planes, but these planes have a random configuration referred to as turbo-stratic. Thus the reinforcing carbon blacks as opposed to graphite, consist of quasi-graphite crystallites along with some random carbon. The height of the crystallites is of the order of 15 Å for most blacks, their width of the order of 20 Å and the layer spacing is somewhat larger than in graphite, approximately 3·5 Å. The particle size of carbon black ranges from about 200 Å for the most highly reinforcing types to a few thousand Ångstroms for the mildly reinforcing thermal carbons. Reinforcing character is also attributed to the presence of surface functional groups on carbon black. It has been observed that deactivation by graphitisation of carbon black does not completely destroy the reinforcing effect of carbon black although it does indeed produce some profound changes as shown in Tables 1 and 2 (Kraus, 1965; Sheffer & Smith, 1955).

There can be no question that graphitisation reduces the ability of the black to reinforce, as evidenced by the tensile strength data, but comparison with the unfilled vulcanisate shows that considerable reinforcement remains.

Graphitisation of carbon black not only removes active sites and renders the surface energetically homogeneous for physical adsorption, but also removes substantially all sites of chemical reactivity. An unequivocal decision as to the cause of diminished reinforcing ability of graphitised black is therefore difficult.

The reinforcing effect of carbon black is governed by its fineness and it is well known that the finer the carbon black, the better it is as a reinforcing filler. With graphite reduction of particle size can only be effected by a mechanical grinding process and it has been observed that, grinding processes to reduce materials such as carbon to a particle size sufficiently small to give reinforcement of rubber, have met with little success (Brenner & Colpitts, 1948). An attempt has therefore been made to survey some of the possibilities of incorporating a micronised form of graphite of particle size less than 40 microns and available locally, as a diluent filler in natural rubber (NR) in order to give the rubber compound some of the desirable properties of graphite such as its chemical and thermal conductivity, heat resistance, chemical stability and its strength in compression, and to forecast areas of application where these special properties of graphite could be made use of.

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TABLE 1

EFFECT OF GRAPHITISATION ON REINFORCING ABILITY OF CHANNEL BLACK IN SBR MIX

Black	300 % M (psi)	TS (psi)	EB (%)
Channel	1380	3908	610
Graphitised channel	290	2840	750
None	140	220	440

COMPOUNDING RECIPE

SBR (1500)	100
Black	50 or 0
Zinc oxide	3
Stearic acid	1
Sulphur	1·75
CBS	1·1
Antioxidant	1

Cured for 40 min at 153°C.

TABLE 2

EFFECT OF GRAPHITISATION ON REINFORCING ABILITY OF HAF CARBON BLACK IN NR MIX

	300 % M (psi)	TS (psi)	EB (%)
HAF black	2750	3750	450
Graphitised HAF black	750	3400	600

COMPOUNDING FORMULATION

RSS	100
HAF black	50
Stearic acid	2·5
ZnO	5·0
S	2·5
CBS	0·5
Antioxidant	1·0

Cured for 40 min at 140°C.

An attempt has also been made to chemically modify the graphite structure by a process of oxidation to form graphite oxide, and to find out whether any improvement in the reinforcing character is achieved.

Experiments centered around graphite has therefore been to find : (*a*) a convenient and effective way of dispersion of graphite in NR, (*b*) to recommend new areas of application where some of the useful qualities of graphite may be harnessed, and (*c*) attempts to chemically modify graphite to improve its usefulness in rubber compounding.

MATERIALS AND METHODS

Dispersion of graphite in NR : One approach to improvement of dispersion of fillers and similar compounding ingredients in rubber compounds has centred around mechanical methods for the dry-mixing of compounding ingredients into the rubber. The other approach is latex masterbatching, or the incorporation of the filler into rubber in the latex stage, followed by recovery of the filler rubber mixture by coagulation or co-precipitation. Dry-mixing of graphite with rubber in the Banbury or the two-roll mill is expected to be difficult due to the very special lubricating power of graphite. However, it was found possible to dry-mix graphite and rubber using a laboratory scale Banbury mixer. Even though slippage was a problem in the two-roll mill, in small scale dry-mixing using batch weights of less than 250 g, no difficulty in mixing was encountered in the laboratory Banbury.

Incorporation of graphite into rubber by the masterbatching technique : The graphite slurry was dispersed using Dispersol LN (ICI), a sulphonate type of dispersing agent. It was preferable to incorporate oil into the masterbatch in order to overcome some of the problems in the subsequent dewatering and drying stages. A 50% oil emulsion based on Dutrex R was prepared using ammonium stearate as the emulsifying agent. A mixture of graphite slurry and oil emulsion in the appropriate quantities required for masterbatching were homogenised by passing at least six times through a homogeniser. The graphite/oil mixture was then mixed with field latex (DRC 33%). Stirring was continued during coagulation with 2% formic acid to avoid any sedimentation.

After complete coagulation, the coagulum was dewatered by compressing between rollers and pressed into the form of a sheet and subsequently dried in an oven at 60– 65°C. Drying was completed in 10—12 hr.

RESULTS

The quality level of the masterbatches were determined in a typical tyre tread compound (Table 3). Levels of graphite ranging from 5 to 45 parts have been used to replace high abrasion furnace black in a typical tyre tread compound. There is a significant loss in modulus at 300% as the level of graphite is increased from 5 to 45%. The reduction in tensile strength is also evident, but the results indicate some reinforcement with graphite. Hardness and resilience properties are not significantly changed with the different levels of graphite in the mix, but abrasion resistance tends to deteriorate as the level of graphite is increased.

It is observed that the quality level of latex masterbatches are inferior to the dry mix compound of the same composition. A sulphonate type of dispersing agent was used in the latex masterbatching and it has been shown by other workers in latex masterbatching, using carbon black, that the type of dispersing agent can influence the quality of the masterbatch (Braendle, 1957).

TABLE 3

FILLER LOADING

HAF black	45	40		35		30		—	
Graphite	—	5		10		15		45	
		A	B	A	B	A	B	A	B
A — Direct addition B — Masterbatching									
M 300% (kg/cm²)	120·1	93·7	81·3	88·4	75·9	71·1	60·2	46·8	28·8
M 500% (kg/cm²)	248·4	232·0	197·2	230·3	188·2	181·5	137·5	106·6	64·8
M 600% (kg/cm²)	—	—	—	—	—	—	—	166·7	105·7
T.S. (kg/cm²)	257·0	247·6	230·3	240·6	232·6	225·5	219·3	190·1	163·2
E.B. (%)	505·0	530·0	575·0	500·0	553·0	535·0	598·0	630·0	685·0
Hardness (B.S.°)	59·5	59·5	57·0	60·5	57·5	60·0	57·5	65·5	49·0
Abrasion resistance (% of SW sample)		114·3	120·3	96·9	97·6	90·6	87·8	74·8	47·8
Mooney viscosity (ML, + 4 at 100°C)	36·0	29·0	38·0	26·5	24·0	24·5	22·0	13·0	8·5
Scorch time (120°C)	13′ 10″	14′ 15″	15′ 30″	14′ 15″	14′ 00″	16′ 00″	15′ 00″	25′ 00″	17′ 00″
Resilience — (Lupke)	59·0	62·5	61·0	64·0	61·5	66·0	64·0	71·2	71·0

Recipe

Rubber	100·0
Filler	45·0
Dutrex R	5·0
Zinc oxide	5·0
Stearic acid	2·0
PBN	1·0
CBS	0·6
Sulphur	2·5

Cured for 40 min at 140°C.

Chemical modification of graphite : Oxidation of graphite has been attempted using strong oxidising agents such as mixtures of $C.HNO_3$ and $C.H_2SO_4$. It is believed that during oxidation C-O-C ether-like bridges are formed between the hexagonal rings. As a result of the formation of four covalent bonds by all or most of the C atoms, it is believed that the layers become buckled.

Oxidised graphite was incorporated into rubber in varying proportions, and its tensile properties determined. There was no significant reduction in tensile strength, even when 12·5 parts of carbon black were replaced by an equivalent proportion of the modified graphite.

DISCUSSION

An application where the use of graphite appears possible is in the field of solid tyres. In the curing of a solid tyre, using a compression mould, the problem of heat transfer to the core of the tyre will become increasingly difficult as the cross sectional area of the tyre increases. A useful purpose served by graphite is that due to its excellent heat conductivity, heat transfer to the core of the compound from the surface of the mould will not be a problem.

Low rolling resistance is a further crucial factor in the selection of solid tyres, and the anti-friction property of graphite can be beneficial in this respect. This particular application does demand high compression strengths and graphite contributes to increase the compression strength of reinforced rubber.

CONCLUSION

Graphite can be successfully incorporated into NR both by the latex masterbatching and dry rubber mixing techniques. A suggested area of application of graphite as a diluent filler in the rubber industry is in the field of solid tyres. In this application upto 10 parts of reinforcing carbon black can be replaced by graphite without any significant loss in abrasion, resilience and hardness properties. Further improvements in the usefulness of graphite as a compounding ingredient in NR can be effected by chemical modification of graphite but these attempts may not prove economically feasible.

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